XLIV.—*Identification and Constitution of Fremy's Sulphazotised Salts of Potassium.*

By Edward Divers and Tamemasa Haga.

Fremy found that a sufficiently concentrated solution of potassium nitrite and hydroxide, when treated with sulphur dioxide, gave minute, silky needles of a salt which he provisionally named *potassium sulphazate*. With a slightly diminished concentration of the solution, he generally obtained, instead of this, the brilliant, often hard, rhombic prisms of *potassium basic sulphazotate* (5/6 normal hydroximidosulphate, Trans., 1894, **65**, 523). Sometimes, however, neither of these salts was obtained before the solution became transformed into a starch-like jelly through the formation of a salt which he named *potassium metasulphazate*, or else became filled with spangles of yet another salt called by him *potassium metasulphazotate*. When the solution was a little too dilute to give any

of these, and if too much alkali had not been added, peculiarly pointed crystals usually appeared consisting of the salt he named *potassium neutral sulphazotate* (2/3 normal hydroximidosulphate, Raschig), and lastly, with still greater dilution, the minute, brilliant needles of the *potassium sulphammonate* (nitrilosulphate, Berglund). He believed also that other salts were produced in the first stages of the reaction, one of which he named *potassium sulphazite*, but this he did not succeed in isolating, assigning as a reason the excessive solubility of the salt. He prepared it—but only in very small quantity and as crystalline, warty granules—by the action of water on the 'sulphazate,' whereby this was converted into 'basic sulphazotate' which was deposited, and a solution that on evaporation yielded the 'sulphazite.' These two salts, if dissolved together, were changed back again into the 'metasulphazotate,' whilst the 'sulphazite' and the 'sulphazate' could similarly often be changed into the 'metasulphazate' again. These two meta-salts he regarded, therefore, as perhaps merely double salts of the others. The 'sulphazite,' the 'sulphazate,' and the 'sulphazotates' he treated as being members of a series of salts in which there were two atoms of nitrogen, and from one up to eight atoms of sulphur,—three in the 'sulphazite,' four in the 'sulphazate,' and five in the 'sulphazotates.' With this conception of the nature of these salts, based on his analyses, it was easy to understand the decomposition of the 'sulphazate' into the 'sulphazite' and the 'sulphazotate.' But this and other of Fremy's interpretations of the facts observed by him have lost all importance and particular interest through the progress of chemistry since his memoir was published.

Subsequent work by others and by us in the same field has shown that Fremy, in the acount he gave of the preparation of his many salts, went too little into details as to the conditions under which they were obtained—apparently because he was not able to be more precise. When Claus attempted to prepare Fremy's salts, he obtained only masses of minute crystals of salts, of whose individuality and nature he could make out but little because of the impossibility of dissolving them entirely without decomposition. In his experiments, the 'sulphammonate' (nitrilosulphate) was always formed in considerable quantity, either as a first or secondary product, and by its presence prevented any satisfactory investigation of the other salts. In Fremy's working, this most easily formed salt came only as the final product of the sulphonation and therefore gave him no trouble. Claus emphatically displayed his scepticism as to Fremy's results; yet in nearly every point in which he differed from Fremy as to the facts, we find Fremy to have been right. When Raschig repeated Fremy's work—*but with the modifications in procedure introduced by*

Claus—he obtained results similar to, although less unsatisfactory than, those recorded by Claus, and he made an approach to Fremy's work in so far as that he often got very little nitrilosulphate; nevertheless, he too failed in his attempts to prepare the 'sulphazate' in Fremy's way.

In perhaps all essential points we can lay down the method to repeat Fremy's experimental work successfully. In some cases, however, a little uncertainty obtains owing to the fact that the very concentrated and complex solutions which yield Fremy's salts are apt to deposit what is virtually the same salt in different forms and also, at times, salts quite distinct from each other; there being only slight and obscure variations in the circumstances attending their formation.

Sulphazate.—This is Fremy's first salt directly obtained in his sulphonation of the nitrite. In getting it, he took approximately 5 mols. of potassium nitrite to 2 mols. of potassium hydroxide and a little water, and into the solution passed sulphur dioxide until it became almost filled with silky needles very soluble in water. So far, it is easy to follow Fremy with a full measure of success, if only the water used is limited to perhaps twice the weight of the nitrite, and that the heating produced by the action is counteracted by cooling. Claus, and after him Raschig, failed, but then inexplicably to us they did not start with Fremy's proportions of nitrite to hydroxide, although even with the proportions they took, success is possible if care be taken. The salt thus formed by Fremy was not tested and analysed by him until after it had been changed (but without his having recognised the fact) by the further treatment to which he submitted it. Before change, it is the potassium nitrito-2/3 normal hydroximidosulphate described in the preceding paper, a neutral salt which is decomposed into its constituent salts by water. Fremy's finished 'sulphazate' was strongly alkaline and very caustic, and when decomposed by water gave nitrite and the 5/6 normal hydroximidosulphate—not the 2/3 normal salt. Also the analysis he gave of it furnished numbers such as the original product could not have given. Instead of potassium, 33·10, sulphur, 18·06, and nitrogen, 7·9 per cent., he obtained potassium, 34·90, sulphur, 19·55, and nitrogen, 4·9 per cent. We can learn what his after-treatment was by reference to other parts of his paper where he speaks of the care necessary (when sulphonating the nitrite) to maintain the alkalinity of the solution by adding potassium hydroxide from time to time, and of dissolving sulphazotised salts, for examination, in water containing this alkali. It seems certain that he must have added some potassium hydroxide to the solution after getting it to crystallise, as a precaution to preserve the salt; now the effect of this addition is to change the composition of the product without much affecting its silky, asbestos-like appearance. The change it

thus undergoes deprives it of much of its nitrite and converts the 2/3 normal into more nearly normal hydroximidosulphate—replacing, therefore, potassium nitrite by potassium hydroxide. Accepting Fremy's mean numbers as accurate, what he analysed had the composition $11K_3NS_2O_7,H_2O$; $K_2HNS_2O_7,2H_2O$; $2(K_2HNS_2O_7,KNO_2)$.

	Potassium.	Sulphur.	Nitrogen.	Alk. potassium.
Found	34·9	19·55	4·9	— per cent.
Calculated ...	34·9	19·51	4·9	9·36 ,,

His analyses, however, have no claim to receive such close treatment, his nitrogen seemingly being always much too low; and it is sufficient to say of his 'sulphazate' that it was the silky, asbestos-like, nitrito-2/3 normal hydroximidosulphate more or less converted into the also silky, asbestos-like normal hydroximidosulphate, and with this Fremy's description of its other properties entirely agrees. With dilute acids, it slowly evolves nitrous oxide unmixed with nitric oxide. Fremy specially points out that no *sulphazic acid* or any other *sulphazates* could be obtained from the potassium salt. There is, therefore, nothing to justify belief in this compound being the salt of a particular single acid, the *sulphazic*.

Sulphazite.—What Fremy named *potassium sulphazite*, he only once obtained (and then not by direct sulphonation of the nitrite) in mammillated, white, crystalline crusts from a solution thickened by the other salts contained in it. That is to say, his *sulphazate* when dissolved in a little water containing some potassium hydroxide, deposited crystals of *basic sulphazotate* (5/6 normal hydroximidosulphate) and left a mother liquor which on evaporation in the cold until it became syrupy yielded the *sulphazite*. It showed great analogy with his *sulphazate*, but was distinguished from it by having little tendency to hydrolyse, and by at once evolving some nitric oxide when its solution was mixed with a dilute acid. Water decomposed the *sulphazite*, but into what products was not ascertained.

We have sufficiently realised Fremy's expectations that his sulphazite might directly result from sulphonating the nitrite with subsequent addition of alkali. The substance obtained in this way did not differ greatly in composition from his:

	Potassium.	Sulphur.
Fremy's salt.....	38·16	16·27 per cent.
D. and H.'s salt ...	36·94	16·37 ,,

and agreed with it in chemical properties, so far as is known. At the same time, it was indistinguishable from a compound of nitrite with 5/6 normal hydroximidosulphate, the third one described by us as such in the preceding paper (p. 436). Other experiments of various

kinds have yielded us such 'mammillated crusts' as Fremy obtained which, although only in rough agreement in percentage composition with his sulphazite, behaved like it, and proved to be impure double salts of nitrite with 5/6 normal or more nearly normal hydroximidosulphate. We are therefore convinced that his sulphazite was merely such a double salt.

*Metasulphazate.**—In Fremy's experience, when passing sulphur dioxide into the solution of nitrite and alkali of a concentration intermediate between that giving *sulphazate* and that giving *basic sulphazotate*, it sometimes happened that the solution set to a starch-like jelly instead of crystallising. He obtained a similar jelly by cooling a hot concentrated solution of *sulphazate* and *sulphazite*; also by boiling a solution of *sulphazate* and then cooling it. When strongly compressed, the jelly became a transparent, wax-like mass. Heated to 50—60° in this waxy state, it suddenly changed into a solution of *sulphazite* and minute crystals of *basic sulphazotate*. In all other respects, it proved to be intermediate in properties between *sulphazate* and *sulphazite*. No other *metasulphazates* could be prepared from it, so that Fremy was disposed to regard it as being a double salt of *sulphazate* and *sulphazite*. Its constitution must therefore have been that of nitrite combined with normal, or 5/6 normal hydroximidosulphate in such proportions and with such additions, perhaps, of alkali as prevented crystallisation.

We have not had Fremy's success in getting this salt in the jelly and wax-like forms, but have met with just such phenomena when forming barium sodium hydroximidosulphate, $BaNaNS_2O_7,H_2O$, as will be found described in our paper already frequently referred to. We have, however, obtained a salt, or homogeneous mixture of salts, of the same composition as the *metasulphazate*, but with the form of the silky, radiating, fibrous crystals of the nitrito-normal hydroximidosulphate, from which it differed only in showing deficiency of nitrite, that is, it was equivalent in composition to a mixture of the normal salt and its nitrite compound, both of which crystallise in the same habit. We give below Fremy's numbers, our own, and those calculated for the expression, $3(KNO_2,2K_3NS_2O_7,4H_2O),K_3NS_2O_7,3H_2O$.

	Potassium.	Sulphur.	Nitrite.	Alk. potassium.
Found (Fremy) ...	35·10	16·74	4·81	— per cent.
„ (D. and H.)	35·10	16·68	—	10·47 „
Calculated	35·06	16·74	5·23	10·23 „

We prepared the salt by dissolving the hydroximidosulphate in hot concentrated nitrite solution containing alkali. To 100 c.c. of water, there were present 45½ grams of nitrite and 1⅔ grams of potassium hydr-

* Often misprinted *metasulphazotate* in the French original, but not in the German translation.

oxide; for 66 mols. nitrite there were dissolved 10 mols. anhydrous normal hydroximidosulphate. Except for the salt being in beautiful, asbestos-like fibres, there was nothing to distinguish it from the jelly and the wax-like *metasulphazate*, which therefore we do not hesitate to class as a nitrito-hydroximidosulphate.

Basic sulphazotate, which Fremy considers next, has been shown by us already (*loc. cit*) to be the 5/6 normal hydroximidosulphate, and not the salt of a distinct acid, the *sulphazotic*. It is liable to contain a small excess of potassium when crystallised from a strongly alkaline solution. A solution of the normal salt readily deposits it, as does also that of the nitrite compound of the normal salt.

Neutral sulphazotate was shown by Raschig to be the 2/3 normal hydroximidosulphate. Fremy distinguished the *potassium sulphazotates* from the salts previously described by him by their ability to form other sulphazotates by double decomposition. Fremy's analytical results in the case of the *neutral sulphazotate* are hopelessly out of accord with its constitution and properties, although those for the *basic sulphazotate* are satisfactory enough.

Sulphazidate, produced by the hydrolysis of the *sulphazotate*, is hydroxyamidosulphate (Claus). *Sulphazilate* and *metasulphazilate*, oxidation products of the *sulphazotate*, are $ON(SO_3K)_2$ and $ON(SO_3K)_3$, and have been studied by Claus, Raschig, and Hantzsch.

Metasulphazotate.—Sometimes Fremy isolated a salt in the form of spangles (*paillettes*), in appearance like minute crystals of basic sulphazotate, but differing from them in not being hard. This salt he named, therefore, *metasulphazotate*. According to him, it can also be obtained by mixing (hot) solutions of the (*basic*) *sulphazotate* and *sulphazite*. It is very soluble in water, very alkaline, and unstable unless the water contains alkali. In pure water, it becomes *basic sulphazotate* and *sulphazite* again. It shows the greatest analogy to *metasulphazate*, and is distinguished from *basic sulphazotate* in the same way. It may be a compound of *basic sulphazotate* and *sulphazite*. So far Fremy. It will be evident that there is nothing in its history or properties to distinguish it, except its occurring in the form of sparkling particles, and even that can be met with in the *basic sulphazotate* suddenly precipitated; we have also obtained other of the sulphazotised salts in what may be called spangles, although not this particular salt. In the preceding paper (p. 434), we have described an impure form of nitrito-2/3 normal hydroximidosulphate, obtained by dissolving the 5/6 normal salt in a hot concentrated solution of nitrite, but still not so concentrated as to give the nitrito-5/6 normal double salt. This preparation is lustreless while in its mother liquor, but when dried on a tile has a fine silvery lustre. It has, when dried in a desiccator,

exactly the composition of Fremy's *metasulphazotate*, and is much less alkaline than the *metasulphazate*. It may be formulated as

$$K_3NS_2O_7 + 9(KNO_2, K_2HNS_2O_7, 1\tfrac{1}{2}H_2O).$$

	Potassium.	Sulphur.	Nitrite.	Alk. potassium.
Found (Fremy).....	33·8	18·6	3·5	— per cent.
„ (D. and H.).....	33·79	18·35	—	1·09 „
Calculated.....	33·68	18·37	7·63	1·12 „

Sulphammonate and *sulphamidate* are respectively nitrilosulphate and imidosulphate (Berglund).